Abstract Linear and nonlinear rheological response of complex fluids is of great interest. Oscillatory techniques are commonly used to analyze the complex fluid rheological behaviour. In this chapter, approach based on large amplitude oscillatory shear (LAOS) is reviewed. Initially, oscillatory shear based on small strains is presented along with a brief discussion on relaxation time spectrum. Subsequently, key observable features of LAOS are shown with example experimental observations on selected materials. Various applications for which LAOS is being investigated has been described through these examples.

Materials such as polymer melts and solutions, emulsions, blends, biological gels, micellar solutions etc are being investigated for their nonlinear response at large amplitudes during LAOS. In addition to the general response during LAOS, specific material functions being proposed in the literature are discussed. Finally, an example of bulk oscillatory flow is discussed in the context of LAOS behaviour of complex fluids.

1 Introduction

Rheological characterization is carried out using several simple controlled methods such as steady shear, stress relaxation, creep, oscillatory shear and steady extension. The results of these tests are quantified using material functions such as steady viscosity, relaxation modulus, creep compliance, storage and loss modulus and extensional viscosity, respectively. For specific materials, other rheological tests have been used frequently. These tests, such as double step shear, stress growth, superimposed oscillations on prescribed strain or stress etc. are more appropriate considering the engineering application or they serve to highlight the effect of molecular or micro-structural features on material response more effectively.

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Oscillatory shear is used widely in characterization of viscoelastic materials [2, 16]. In this method, both stress and strain vary cyclically with time, with sinusoidal variation being the most commonly used. This is the most popular method to characterize viscoelasticity, since relative contributions of viscous and elastic response of materials can be measured. The cycle time, or frequency of oscillation, defines the timescale of these tests. By observing material response as a function of frequency, material can be probed at different timescales. This observation of material response at different frequencies is also referred to mechanical spectroscopy. The overall material response is due to contributions from several mechanisms at the molecular and microscopic levels. A set of timescales can be identified with each mechanism. The ratio of the two timescales, the experimental and material, can be varied by observing response at different frequencies.

1.1 Small amplitude oscillatory shear

We can represent the sinusoidal strain applied to a complex fluid sample as,

$$\gamma = \gamma_0 \sin \omega t .$$

(1)

The linear response of material in terms of stress can be written as

$$\sigma = \sigma_0 \sin (\omega t + \delta) ,$$

(2)

where $\delta$ is the phase lag. The response given by the above equation is usually observed at low amplitudes of strain ($\gamma_0$). At larger strain and/or stress amplitudes, the nonlinear response of materials is discussed later. Different waveforms, such as triangular, square, trapezoidal etc. have also been used in oscillatory shear.

In small amplitude oscillatory shear (SAOS), based on the strain imposed and the stress response, material functions are defined to quantify the material behaviour. For example, storage ($G'$) and loss ($G''$) moduli are defined as ratios of stress and strain amplitudes. Storage modulus is based on the amplitude of in-phase stress and loss modulus is based on the out-of-phase stress. Based on these material functions, Eq. 2 can be written as,

$$\sigma = G'(\omega) \sin \omega t + G''(\omega) \cos \omega t ,$$

(3)

A primitive model to describe viscoelastic behaviour of materials is the Maxwell model,

$$\sigma + \lambda \frac{d\sigma}{dt} = \eta \dot{\gamma} ,$$

(4)

where $\lambda$ (the relaxation time) and $\eta$ are the model parameters. $\lambda$ is the characteristic time of material response. Large values of $\lambda$ imply elastic response, while
small values imply viscous response. $\eta$ is the characteristic zero shear viscosity. When subjected to SAOS, the response of Maxwell model is,

\[ G' = \frac{\eta \omega^2 \lambda}{1 + \omega^2 \lambda^2}, \quad G'' = \frac{\eta \omega}{1 + \omega^2 \lambda^2}, \quad (5) \]

As can be observed from the above equation, material response at very low frequencies is $G' \propto \omega^2$ and $G'' \propto \omega$, signifying viscous response. At very high frequencies, material response is $G' = \eta / \lambda$ and $G'' \propto \omega^{-1}$. The constant value of storage modulus is $G = (\eta / \lambda)$, and is called the elastic modulus. The crossover between $G'$ and $G''$ occurs at the frequency $\omega = 1 / \lambda$. A complex modulus, $|G^*| = \sqrt{G'^2 + G''^2}$, is also sometimes used for analyzing the behaviour. Using complex notation, applied sinusoidal strain can be written as,

\[ \gamma = \gamma e^{i\omega t}. \quad (6) \]

If the above strain is applied and for the case of linear response, one can write

\[ \sigma = G^* \gamma. \quad (7) \]

As we will see later, the above equation can be seen as the truncated form (upto the linear term) of the overall relation between stress and strain. Either stress or strain can be visualized as the excitation and consequently, either strain or stress can be visualized as the response. The results of oscillatory shear tests are presented in different ways for analyzing the data. An example is plot of $G''$ Vs $G'$ or the Cole-Cole plot. Response of Maxwell model, as given by Eq. 5, on Cole-Cole plot is represented by a semi-circle with center at $(G/2,0)$ and radius of $G/2$. Plots of $G^*$ Vs $\delta$ are also used to analyze the property variation.

The cyclic variation of stress and strain can be observed by plotting them against each other. For fluids, stress and strain rate are also plotted. Examples of stress-strain variation, also called Lissajous plots, are shown in Fig. 1. Stress and strain are in phase for elastic materials (maximum stress when strain is maximum etc) leading to a straight line on this plot, in case of linear elastic materials. On the other hand, they are out of phase ($\pi/2$) for viscous materials (implying maximum stress when strain rate is maximum). This behaviour is represented by a circle in the plot, if the fluid is linear viscous or Newtonian. For a viscoelastic material, with a phase lag $0 < \delta < \pi/2$, the stress strain curve is elliptical.

Similar plots of stress–strain rate would result in a straight line for linear viscous response, circle for linear elastic response and an ellipse for linear viscoelastic materials.

The linear elastic and linear viscous responses are represented by straight lines or circles. For nonlinear elastic or nonlinear viscous materials, these plots would be nonlinear curves instead of straight lines or they would ellipses (with major and minor diameter coinciding with axes) instead of circles. Before discussing such response nonlinear viscoelastic behaviour, typical examples of response to SAOS is discussed.
1.2 Typical response

Example variations of $G'$ and $G''$ are shown in Fig. 2 for a polymer melt, emulsion and a crosslinking polymer. For the polymer melt (Fig. 2(a)), at very low frequency, viscous behaviour is observed. At higher frequencies, the behaviour is largely governed by the entanglements between polymer molecules. This region is also referred to as the plateau region, due to relatively constant moduli. At very high frequencies, the response is almost elastic. This response is also referred to as the glassy behaviour. It should be noted that the change from viscous to elastic behaviour is observed over a couple of decades in frequency (a change of 100) in case of Maxwell model. However, for most materials this change, if at all observed, occurs over several decades. For polymer melts, the moduli change by 7-8 orders of magnitude for a 7-8 orders of magnitude change in frequency.

The rheology of the emulsions is strongly influenced by the state of flocculation [9]. Unflocculated or weakly flocculated emulsions show a crossover point between $G'$ and $G''$. This crossover frequency is associated with a characteristic relaxation time for the onset of the terminal or flow region for the emulsion. Highly concentrated stabilized emulsions show a gel-like response, implying $G'$ to be larger than $G''$ and both being almost constant with respect to frequency. Fig. 2(b) shows the normalized response of emulsions (with different stabilizer concentrations). As mentioned, $G'$ is larger than $G''$. Both change by an order of magnitude in the range of frequencies investigated [9]. Therefore, a plateau-like region can be observed as the overall response. Similar to the entanglement plateau region in case of polymer, this region in emulsions may be due to interactions between emulsifiers from neighbouring droplets [9].

Fig. 2(c) shows evolution of linear viscoelastic response for a sample undergoing gelation. In this case, sodium acrylate is being crosslinked in the presence of free-radical crosslinker. Initially, $G'$ is observed to be lower than $G''$. With crosslinking reaction and network formation, both $G'$ and $G''$ increase. Near the gel point, there
is a crossover in $G'$ and $G''$ and subsequently $G'$ is larger than $G''$ [10]. Once the reaction is complete and gel is formed, both $G'$ and $G''$ become constant. $G'$ and $G''$ for the gel are almost independent of frequency.

The overall response to SAOS, as exemplified in Fig. 2 is very complex compared to simplistic response exhibited by Maxwell model, which is characterized by a single relaxation time. We understand the overall response by analyzing it to be due to combinations of several relaxation times.

1.3 Relaxation time spectrum

The overall material response is visualized in terms of combinations of several mechanisms and modes. Each of the modes is described in terms of a Maxwell model. Therefore, overall response of material can be captured through a combination.

![Moduli vs Frequency](image)

**Fig. 2** Representative oscillatory shear response: (a) polymer (b) oil in water emulsions [9] (c) evolution during gelation [10]
nation of Maxwell models (or generalized Maxwell model) with each mode corresponding to a relaxation time. The strength of each mode may also be different. The relaxation modulus for Maxwell model is given by,

$$G(t) = G_0 \exp \left( -\frac{t}{\lambda} \right),$$

(8)

For material response with several Maxwell modes, the relaxation modulus is,

$$G(t) = G_e + \sum_i G_i \exp \left( -\frac{t}{\lambda_i} \right),$$

(9)

where $G_e$, equilibrium modulus is zero for fluidlike materials, and $G_i$, elastic modulus and $\lambda_i$ are elastic modulus and relaxation time for $i^{th}$ mode. Based on the above equation, we can define a relaxation time spectrum, $H(\lambda)$ as,

$$H(\lambda) = \sum_i G_i \delta(\lambda - \lambda_i).$$

(10)

Therefore, relaxation modulus can be written in terms of the relaxation time spectrum as,

$$G(t) = G_e + \sum_i G_i \delta(\lambda - \lambda_i) \exp \left( -\frac{t}{\lambda} \right).$$

(11)

Similarly, we can define the relaxation modulus based on the continuous relaxation time spectrum as,

$$G(t) = G_e + \int H(\lambda) \exp \left( -\frac{t}{\lambda} \right) d\lambda.$$

(12)

The storage and loss moduli can be written in terms of relaxation time spectrum as follows,

$$G' = \sum_i \frac{G_i \omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2}, G'' = \sum_i \frac{G_i \omega \lambda_i}{1 + \omega^2 \lambda_i^2}$$

(13)

Alternately, in terms of continuous spectrum,

$$G' = \int \frac{H(\lambda) \omega^2 \lambda}{1 + \omega^2 \lambda^2} d\lambda, G'' = \int \frac{H(\lambda) \omega}{1 + \omega^2 \lambda^2} d\lambda$$

(14)

Based on these equation, relaxation time spectrum can be estimated from data such as in Fig. 2 and the mechanisms of material behaviour can also be understood in terms of the distribution of relaxation times.

An example of discrete relaxation time spectrum (referred to as PM spectrum in the figure) evaluated from oscillatory shear data is shown in Fig. 3. These data are for different molecular weights of monodisperse polybutadiene samples. Analytical expressions for relaxation time spectrum have also been proposed and one example is (BSW spectrum in the figure) [1].
where $\lambda_1$ is the shortest measurable relaxation time and $\lambda_{\text{max}}$ is the largest relaxation time of the polymer. When tested below $1/\lambda_{\text{max}}$ (i.e. at strain rate or frequency lower than this value), polymer would show Newtonian viscous behaviour. $H_e$, $n_e$ and $H_g$, $n_g$ are coefficients to capture the entanglement modes and glassy modes of the polymer, respectively.

Examples of relaxation time spectrum for polymers and an emulsion are given in Fig. 1.3. As was observed in Fig. 2 with $G'$ and $G''$, there is marked difference in the relaxation time spectrum for both the materials.

As discussed in Sects. 1.1–1.3, material response can be described in terms of microscopic mechanisms. These mechanisms for complex fluids, such as poly-
mers, colloids, gels, liquid crystals, micelles etc, are recognized based on microscopic/molecular cooperative organization [17]. The viscoelastic behaviour in the linear and nonlinear regimes is dependent on how the organization responds to deformation.

1.4 Linear and nonlinear response

The response is termed linear if scaled change in input leads to change in the output with the same scaling. Describing linear response in other words, the output of a combination of inputs is the same as the combination of outputs of individual inputs. This is also referred to as superposition principle. In the context of SAOS, if the strain amplitude is changed by a factor, the stress amplitude of the sinusoid also changes by the same factor. Therefore, material functions such as $G'$ and $G''$ are not functions of strain amplitude. The linear viscoelastic limit (or the maximum strain amplitude at which linear viscoelastic behaviour is observed) can be found by measuring the material functions as functions of strain amplitude.

The onset of nonlinear response is therefore, expected at larger amplitudes of strain/stress as discussed in Sect. 2. Nonlinear response, in the context of rheological response, can be classified as due to large deformations, structural changes and phase transitions [18]. Analysis of nonlinear response is complicated, because interplay of these factors is difficult to resolve and their mathematical representations are difficult to propose and solve. However, in recent decades, lot of progress in theoretical and experimental tools has led to significant understanding. The use of oscillatory shear in the nonlinear regime is an example of such endeavour.

As in the case of linear viscoelastic behaviour, several methods can be used to examine the nonlinear response of the materials. These include creep and recovery, stress relaxation, oscillatory shear etc. These different methods serve to highlight particular structure-property relations or they are more relevant for an application. Along with experimental characterization, development and use of comprehensive models that explain behaviour of different materials in various methods of probing are continuously being undertaken.

1.5 Susceptibility

Linear and nonlinear response of materials to excitation is of interest in various fields such as mechanical, electrical, thermal and their combinations. The material property relating the response and excitation is referred to as susceptibility. At low levels of excitation, linear response is observed. In other words, the implication is (in case of oscillatory excitation) that the susceptibility is independent of the amplitude of excitation.
Linear response is usually very important in understanding basic mechanisms responsible for material behaviour. Nonlinear response, on the other hand, is more relevant for applications and is also more difficult to characterize. Measuring the nonlinear response of a material to an excitation is a way to examine properties, which cannot be characterized by examining the linear response. Understanding nonlinear effects has led to breakthroughs in different materials such as elastic, plastic, viscoelastic, optical materials, ferroelectric, freezing, or dipolar glass transitions, isotropic-liquid crystal transition or binary mixtures, superconductivity, field or heating effects in electrical transport, heating due to electric field excitation of supercooled liquids [24].

Similar techniques are used for the analysis of nonlinear response in these diverse areas. As an example, the response in dielectric spectroscopy and mechanical spectroscopy can be understood in relation to each other. For small amplitude of electric field, similar to Eq. 7, we can write the relation between electric displacement ($D$) and electric field ($E$) as,

$$D = \varepsilon^* E,$$  \hspace{1cm} (16)

where $\varepsilon^*$ is permittivity of material. The modes of material response, as discussed in earlier sections, can also be identified by examining the dielectric response as a function of frequency. In case of rheology, load and displacement are measured and analysis is carried out for stress, strain or strain rate. In case of dielectric response, we measure current and voltage and carry out the analysis with electric field, polarization or electric displacement.

When material is subjected to large amplitude of electric field, the above equation is no longer valid. However, material behaviour can be described by writing higher order terms in electric field [3],

$$D = \varepsilon_1^* E + \varepsilon_2^* E^2 + \varepsilon_3^* E^3 + \ldots,$$  \hspace{1cm} (17)

where $\varepsilon_n$ is the permittivity of $n^{th}$ order. It can be shown that only the odd powered terms of the above equation are non-zero. In addition to such general descriptions, variety of theoretical and experimental tools are common in investigations of nonlinear response of materials. In the next few sections, various features of nonlinear response in oscillatory shear will be described.

### 2 Oscillatory testing at large amplitude

The classes of overall oscillatory rheological response of materials can be understood from the diagram shown in Fig. 4. The diagram (referred to as Pipkin diagram) can be recast in the form of dimensionless numbers, Weissenberg number ($We = \dot{\gamma} \lambda$) and Deborah number ($De = \omega \lambda$). At low frequencies, and at low strain amplitudes, the material response is purely viscous and Newtonian. As mentioned earlier, this is at timescales larger than the largest relaxation time in the ma-
material. With an increase in frequency, we observe viscoelastic response at timescales smaller than the largest relaxation time in the material. Depending on the strain amplitude or strain rate amplitude, a crossover from linear viscoelastic to nonlinear viscoelastic is observed. At low frequencies, this crossover occurs beyond a threshold of strain rate amplitude, while at high frequencies, it occurs beyond a threshold of strain amplitude. At very high frequencies, with timescales shorter than the smallest relaxation time of the material, all modes are frozen and an elastic response is observed.

The most common nonlinear viscoelastic measurement is steady shear viscosity (where at different strain rates, steady stress response of the material is measured). Using this, we can distinguish different types of behaviour such as shear thinning, shear thickening etc. The material behaviour, as captured by steady viscosity, is not dependent on the direction of rotation; \[ \eta = \eta (\dot{\gamma}) = \eta (-\dot{\gamma}) \].

The most common linear viscoelastic measurement is based on oscillatory shear, as defined in Sect. 1. Most engineering applications may neither involve steady flow nor small deformation. Therefore, large amplitude oscillatory shear (LAOS) is suggested to investigate transient behaviour of the material at large deformations. It can also be used to quantify the progressive transition from linear to nonlinear rheological behavior. At larger amplitudes of strain, oscillatory shear response will be nonlinear viscoelastic and has been investigated for last couple of decades. However, only in recent few years, LAOS is being used to elucidate specific features of different materials. Some of these examples are described briefly in Sect. 4.

![Fig. 4 Diagram showing material response at different frequencies and strain rates](image-url)
2.1 Qualitative description during LAOS

In SAOS, the material response, in terms of stress, is periodic as given in Eq. 2. The strain amplitude limit for observation of linear viscoelastic response (below which SAOS is usually performed) is small. For many materials, it is less than or around 1%. Larger amplitudes, on the other hand imply, strain amplitudes in the range of 10–400%.

When material is subjected to LAOS, the overall stress response has been observed to be periodic as well. In both SAOS and LAOS, a certain number of cycles are required before the terminal steady behaviour is observed (implying cyclic response to be same for \(n\)th and \((n + 1)\)th cycle). The analysis, in both cases, is carried out once the terminal steady behaviour is reached.

The overall frequency of the terminal periodic response, in case of LAOS as well, is largely the input frequency of the strain. When we take a closer look at the cycle, the stress sinusoid may be narrower or wider near the peaks when compared to response if a single frequency response were observed. Additionally, the symmetry before and after the peak may not be present [8]. Similar features are shown when the material is subjected to a given stress and strain response is observed [20]. This qualitative response implies that stress response is not governed only by the sinusoidal behaviour at the input strain frequency. Therefore, stress response can be visualized as being composed of various frequencies. The breaking of the before and after stress symmetry also implies that phase differences exist among response at various frequencies.

Example sinusoidal response during LAOS is shown in Fig. 2.1 (a,b). Though all the features mentioned above are shown in the figure, the response, at first glance, may not seem very different. Indeed, the effect of various experimental errors has to be carefully considered while analyzing the LAOS data. This is discussed further in Sect. 2.4.

Fig. 2.1 also shows another example of deviation from SAOS cyclic response. In this type of response (measured for a concentrated suspension [20], there is a departure from SAOS behaviour during part of the cycle. Significant deviations in strain rate are observed during reversal of flow direction, i.e. when strain starts increasing from the minimum value or when strain starts decreasing from maximum value.

Based on this basic description of cyclic response during an LAOS experiment, following features can be used to quantify the material response:

**Amplitudes of stress and strain:** The magnitude of first harmonic as function of strain amplitude or ratio of stress and strain amplitudes can be examined for storage and loss moduli. These properties capture the material response at the same frequency as the input frequency. These measurements are routinely made to find the range of linear viscoelastic response of a material. In these measurements, one can visualize stress response to be written in the form of,

\[
\sigma = \sigma_0 (\gamma_0) \sin(\omega t + \delta),
\]

(18)
The above equation states that material response to LAOS is modified (when compared to that to SAOS) by only the amplitude of stress being dependent on the strain amplitude. The sinusoid is represented by the same function in SAOS and LAOS. When $\sigma_0 \sim$ constant, linear viscoelastic response or SAOS behaviour is observed.

The onset of nonlinear behaviour and subsequent variation as a function of strain amplitude has been examined for a large class of materials. An example result is shown for poly sodium acrylate gel and cellulose microfibrils / poly sodium acrylate gel in Fig. 6. It can be observed that the onset strain (for the nonlinear response) decreased in the presence of microfibrils.

As another example, the onset strain has been related to the structure of a colloidal gel [23]. The structure of polymeric solutions and intermolecular interactions in them can be distinguished based on this response [13]. The decrease in $G'$ and $G''$ with strain amplitude, as shown in Fig. 6 is referred to as strain softening. Additionally, depending on the material, one case observe increase in $G'$ and $G''$ (strain hardening) and overshoots in $G'$ and $G''$ followed by decrease [13]. These changes correspond to changes in stress amplitude $\sigma_0(\eta_0)$ (Eq. 18).

**Stress Vs strain during a cycle - Lissajous plot:** As shown in Fig. 1, the stress–strain curves for viscoelastic material subjected to SAOS would be ellipses with different major and minor axes, depending on the relative contributions of viscous and elastic responses (in other words, depending on amplitude of stress response and its phase difference with strain).
The stress–strain curves, in case of LAOS are departure from ellipses. This can be understood based on the qualitative features shown in Fig. 2.1. The departure from linear response (or the response at the input frequency) is exhibited as stretched and deformed ellipses. The response being considered is stress–strain, and therefore this departure is described again in terms of softening and/or hardening of the material during a cycle.

LAOS response can therefore be examined through stress–strain or stress–strain rate plots. Examples of these are shown in Fig. 2.1. The plot shown in Fig. 2.1(a), is for a vanishing cream. As can be seen, there is significant departure from linear viscoelastic response (or elliptical plot). At larger strains in a cycle, proportionally larger stress is required for higher strain and therefore this behaviour is referred to as strain hardening during the cycle.

Stress–strain curves for mucus gel [7] at different strain amplitudes are shown in Fig. 2.1(b). Variation of \( G' \) and \( G'' \), for the various strain amplitudes was observed to be minimal. Therefore, little departure from linear response as described in the first feature, was observed. However, when Lissajous plots are observed (Fig. 2.1(b)), one can notice a striking departure from linear viscoelastic behaviour. Only at low amplitudes (shown in inset), one can observe the elliptical plots.

Another example of cyclic response during LAOS is shown for a concentrated particulate suspensions [20]. The data, which corresponds to Fig. 2.1(c), have been shown with stress–strain rate plot. A linear plot would indicate viscous response, with stress and strain rate in phase. As mentioned earlier, departure from this behaviour is observed during certain duration of the cycle.

**Frequency spectrum:** Fourier transform of the time domain signal is used to evaluate the frequency spectrum. The magnitudes of the peaks at higher harmonics can be used to quantify the nonlinear response of materials.

The deviations from a sinusoidal response with a single frequency (input frequency) can be captured by analyzing the signal as a combination of several frequencies [25]. This is shown in Fig. 8 with the Fourier Transform of the time domain signal. As will be discussed later, higher harmonics (multiples of input frequency)
are observed. The intensities of higher harmonics is much less than the first harmonic (or the input frequency). It should also be noted that the phase difference between strain and various harmonics of stress can be different. Therefore, amplitude and phase of each harmonic are independent characteristics of the material.

The dependence of $G'$ and $G''$ on strain amplitude signifies nonlinear viscoelastic response. The distortion of stress-strain loops (from elliptical shapes) is an indication of nonlinear behaviour. Similarly, the presence or absence of higher harmonics in the material response can be used as an indicator of nonlinear or linear response. However, it is also important to get quantitative measures from all of these measurements. Couple of the quantitative measures, being proposed as nonlinear material functions are discussed in Sect. 2.3. Additionally, it is important to relate the nonlinear response as captured by LAOS to physico-chemical processes in the material. Therefore, simulation of LAOS response with different constitutive models is also an important area of activity.

![Lissajous plots showing (a) nonlinear viscoelastic behaviour [7] (b) deviation from viscous behaviour [20]](image_url)
2.2 General response in LAOS

When a material is subjected to strain as given in Eq. 1, the general stress response of the material can be written as,

\[ \sigma(t) = \sum_{n=1}^{N} \sigma_n \sin(n \omega t + \delta_n), \]  

(19)

where \( \sigma_n \) and \( \delta_n \) are amplitude and phase lag of the \( n^{th} \) harmonic. In this equation, \( \sigma \), a function of time, is being expressed as a Fourier series. In case of linear viscoelasticity or SAOS, only the first term of this series exists (Eq. 2).

The expression for stress can also be written as a series using complex notation,

\[ \sigma = \sum_{n=1}^{N} G_n^{*} \gamma^n. \]  

(20)

For linear viscoelastic response, only the first term of the summation exists (Eq. 7). Similar to storage and loss modulus in case of linear viscoelastic response, we can define a series of storage and loss moduli \( G_n' \) and \( G_n'' \), corresponding to \( n^{th} \) harmonic in the series in Eq. 20. These moduli can also be written in terms of \( \sigma_n \) and phase \( \delta_n \) from Eq. 19.

For isotropic liquids and given that viscosity is not a function of direction of strain rate, it can be shown that only the odd harmonics of the above series are non-zero. This is also the case for dielectric properties, where dielectric constants are not functions of the direction of electric field. The overall number of terms, \( N \) can be arbitrarily large. However, most measurements have been made up to the fifth harmonic due to experimental limitations. The issues related to detection of higher harmonics are discussed later in Sect. 2.4.

The measurement of stress, through the torque or force sensors of the rheometer, are done discretely at a finite sample interval \( (t_s) \). Based on the sampling frequency \( (N_s = 1/t_s, \) number of data points per second), we obtain a time series of discrete measurements. This time domain series can be denoted as,

![Fig. 8](image)

Fig. 8 (a) Time domain signal and the corresponding (b) Fourier transform [25]
\[
\sigma(t) = \sum_{k=1}^{N_s T} \sigma(k) \delta(t - t_k),
\] (21)

where \( k \) takes integer values from 1 to \( N_s T \) and \( T \) is the total duration of measurement. Alternately, the series can be written as \( \sigma(kt_s) \), where \( k = 1, 2, 3... \)

Discrete Fourier transform of this time domain series will also be a series of \( N_s T \) complex numbers. The maximum frequency in the Fourier domain corresponds to Nyquist frequency \( = 2\pi (1/2t_s) \). With the property of Fourier transform leading to meaningful \( N/2 \) terms (symmetric), the resolution in frequency domain is \( 2\pi (1/2t_s) \times (1/(N_s T/2)) = 2\pi (1/T) \). Therefore, sampling interval determines which information can be obtained, while duration of measurement determines the resolution of frequency. Larger \( T \) also leads to higher signal to noise ratio [26].

In the Fourier domain, the intensity of \( n^{th} \) harmonic peak is indicated by \( I_n \). The algorithm for identification of higher harmonics has to consider the resolution in the frequency domain, as the frequency spectrum will not have frequencies which are integral multiples of each other.

This general description will be useful for understanding material behaviour if we can propose quantitative measures based on the evaluated variables. Though LAOS is being investigated for couple of decades, only in recent times we have the theoretical and experimental tools to attempt quantifying the response. In the next section, couple of examples of such quantification are discussed.

2.3 Proposed material functions in LAOS

The moduli \( G_n^\prime \) as defined in previous section are based on the \( n^{th} \) harmonic. Whenever, we analyze one of these moduli, we do not examine the overall response, but look at overall response as contributions from these individual moduli. Based on the time series of stress, moduli can be defined which are not based on an individual harmonic alone [7],

\[
G_L^I = \left( \frac{d\sigma}{d\gamma} \right)_{\gamma=0},
\]

\[
G_M^I = \left( \frac{d\sigma}{d\gamma} \right)_{\gamma=\gamma_0}.
\] (22)

These moduli will reduce to \( G' \) in case of SAOS (linear viscoelasticity). Additionally, they have geometric interpretation as shown in Fig. 9.

Other approaches are based on the ratios of intensities of higher harmonics and first harmonic of the stress response. For example, coefficient \( Q \) is defined as [14],
This coefficient has been claimed to be helpful in distinguishing molecular architecture of polymers based on LAOS. Through analysis of shapes in Lissajous plots and Fourier spectra, such material functions are defined. It should be noted, however, that these material functions will prove useful provided they give insight into material behaviour and help in identifying the microscopic mechanisms involved. Therefore, physical interpretations of these material functions are still being proposed and applied to different complex fluids to examine their utility.

### 2.4 Experimental issues

In general, oscillatory rheological measurements are difficult at very low and high frequencies. At very low frequencies, with lower deformation and strain rates, signal to noise ratio is low due the sensitivity of sensors (or least count). At higher frequencies, inertia effects are significant, while the rheometric analysis assumes absence of these. Mechanical and electrical disturbances during the operation of the rheometer can also lead to errors, which may be significant during analysis of higher harmonics in LAOS [26].

The presence of higher harmonics during oscillatory shear is not always due to terminal nonlinear response of the materials. One has to be careful about contributions from sample inertia [5]. It has been shown that during startup of oscillatory flow (during the time before the terminal steady state is reached), higher harmon-
ics are observed. Therefore it is essential to establish the terminal periodic response before analyzing the LAOS data [8].

Due to small gaps of rotational rheometer geometries, it is assumed that flow is one dimensional with tangential velocities. However, at large amplitudes and at the edges of the geometries, secondary flows can develop. These may also lead to seeming deviation from linear viscoelastic response or the appearance of higher harmonics. A homogeneous flow is also assumed (with constant velocity gradient, or strain rate) across the depth in the rheometer geometry. During LAOS, the flow may become inhomogeneous (shear banding; regions of different strain rates) and therefore, analysis of steady terminal response would be very difficult [17].

Even though the presence of even harmonics is ruled out due to material symmetry considerations, they have been observed in several cases [4, 7]. These even-harmonic terms can be observed due to transient responses, secondary flows, viscous heating or dynamic wall slip. As an example, they have been shown to arise due to misalignment of top and bottom geometry [4]. Edge fracture has also been shown to lead to higher harmonics including even ones [17].

The intensity of \((n+1)\)th harmonic is usually in the range of 1–10% of the \(n\)th harmonic. Therefore, intensities of successive harmonics are very low and it is difficult to ascertain their significance. Due to these experimental issues, LAOS data need to be examined very closely before physical interpretation of material response.

3 Constitutive models and LAOS

The linear viscoelastic models such as Maxwell, Jeffrey’s, standard linear solid and generalized Maxwell model (combination of Maxwell model as described in Sect. 1.3 are commonly used to describe the oscillatory shear response [2, 16]. Some of the simplistic phenomenological models for large deformations or nonlinear viscoelasticity can be considered as extensions of the linear viscoelastic models. For example, upper convected Maxwell model is,

\[
\sigma + \lambda \left( \frac{\partial \sigma}{\partial t} + \mathbf{v} \cdot \nabla \sigma - (\nabla \mathbf{v})^T \cdot \sigma + \sigma \cdot \nabla \mathbf{v} \right) = \eta \dot{\gamma},
\]

where the partial derivative from Eq. 4 has been replaced with upper convected derivative (given in the parenthesis in the above equation).

The quasi-linear model such as upper convected Maxwell model or Lodge rubber-like liquid and Oldroyd–B model lead to linear shear stress response for SAOS as well as LAOS [5, 21]. Therefore, they predict single harmonic stress response, at the same frequency as the strain. However, normal stress differences are predicted to exhibit second harmonic [5] even at small strains. Additionally, all these models predict the presence of higher harmonics during the initial stages of LAOS (before the terminal periodicity is established). These results are not surprising since, the quasi-linear models exhibit no shear thinning behaviour. As is ap-
parent from cyclic response in Fig. 1 and Fig. 2.1, nonlinear viscous and nonlinear elastic behaviour are required to observe hardening/softening during a cycle.

In terms of molecular/microscopic theories, these models can be considered to have fixed entanglement network. Models which consider the transitory nature of entanglement network are, therefore, essential to capture the LAOS. To understand the quantitative variation of stress, several molecular based models and phenomenological models are being used to analyze the LAOS.

It has been shown that many of prevalent constitutive equations show the following scaling for intensity of \( n^{th} \) harmonic with strain \([19, 29]\),

\[
I_n \propto \gamma_n^0,
\]

(25)

The models such as Giesekus, Phan Thien Tanner, Finitely extensible Nonlinear Elastic-P, Marrucci, Leonov, Pom-Pom model show the behavior given by the above equation \([7, 19]\). The degree of shear thinning can be enhanced or reduced based on the parameters of these models. Attempts are being made to understand the LAOS response for different values of these parameters. In various experimental observations and simulations with the above models at very large amplitudes (>100%), departures from Eq. 25 have been reported.

Some of these studies highlight that models which are good for nonlinear viscoelastic behaviour of complex fluids (exhibiting shear thinning, strain hardening in extensional flow, stress growth etc) may not yield quantitative comparison with experimental observations. Progress is needed on both the factors of limited understanding of the response of microscopic mechanisms to LAOS and limited interpretations of experimental measurements.

4 LAOS: Examples

The following list provides a few examples of material systems and specific issues that have been examined with LAOS:

- Examine morphology of polymer blend \([4]\), probing of dispersed phase size distribution
- Effect of flow on drop shape in emulsions of Newtonian fluids \([28]\)
- Concentrated particulate suspension \([20]\)
- Effect of long chain branching on oscillatory shear behaviour \([8]\)
- Effect of oscillatory shear on entanglement dynamics in polymers \([22]\)
- Strain rate frequency superposition in soft solids \([15]\)

Two examples, based on material functions defined in Eqs. 22 and 23, are given in the following discussion.

Material functions for mucus (Lissajou plots shown in Fig. 2.1) are shown in Fig. 10 \([7]\). The response of the first harmonic shows not very significant change (a slight decrease) with strain amplitude, while moduli defined in Eq. 22 show different response. The first observation would lead to a conclusion that near linear
viscoelastic behaviour is observed for almost the whole range of amplitudes investigated. Qualitatively, this behaviour can be described as slightly softening behaviour. However, based on $G'_L$ and $G''_M$, one can observe that softening/hardening behaviour is quite significant and this was also apparent from Lissajous plots.

Fig. 4 shows LAOS measurements on linear and branched polymer melts [12]. The ratios of third harmonic to first harmonic ($Q_{20}^\gamma$), as defined in Eq. 23 were measured for several linear and branched polymers and their blends. Based on simulations with several models (as shown in Eq. 25), we expect this ratio to scale as $\gamma^2_0$. Indeed, for many polymeric melts and other materials, this has been observed. However, as the figure shows, presence of long chain branching leads to a slope $< 2$.

Based on these measurements, it is proposed that in addition to extensional measurements, LAOS can be a useful tool to assess the effect of branching on rheological response of a polymer melt [12]. Pom-Pom model, developed to describe the behaviour of branched polymers, also does not capture the departure of scaling from 2. Therefore, such results also point to the challenges in constitutive modeling of complex fluids under LAOS.

4.1 Bulk oscillatory flow

In this section, an example of bulk oscillatory flow is presented. Fig. 12 shows a cavity (a rectangular box) filled with a given fluid. The top surface of this cavity is moved periodically in x-direction. The filled fluid, at each point in the cavity, is also expected to have periodic velocity. This cavity was used to examine flow of different Newtonian and viscoelastic fluids.

A reactive flow, the gelation of sodium acrylate was carried out in this cuboidal cavity with the top surface undergoing sinusoidal periodic motion. The instantaneous two-dimensional planar velocity fields during gelation were obtained using

![Elastic moduli as a function of strain amplitude for mucus (7)](fig10.png)
Particle Image Velocimetry [11]. Initially, the reaction mixture consists of monomer only, and therefore behaves as Newtonian fluid. However, as crosslinking reactions progress, viscoelastic behaviour is developed (as shown in Fig. 2(c)). The periodic variation of velocities at different points was further examined by obtaining Fourier transforms of the velocities’ time series.

Fourier transforms of \( x \) and \( y \)-components of velocities at a point are shown in Fig. 13. These Fourier transforms were collected at different times after introduction of the initiator. These results show that point velocities fluctuate at higher harmonics during the time of reaction. It is interesting to note that such higher harmonics were observed neither with Newtonian glycerol/water mixtures nor with viscoelastic polyacrylamide/water mixtures.

Nonlinear response arising out of structural changes has been highlighted in the context of LAOS by showing appearance of higher harmonics during crystallization in a polymer melt [6]. It will be interesting to examine if such behaviour is observed during LAOS experiments during gelation.

![Fig. 11 Scaling of \( I_3/I_1 \) with strain amplitude for different (a) linear and branched polymer melts and (b) their blends [12]](image)

![Fig. 12 Periodically driven cavity to observe bulk oscillatory flow](image)
5 Summary

Nonlinear response of complex fluids is very important for most applications. In last couple of decades, nonlinear response is being examined through various approaches. Oscillatory rheology at large amplitudes has been shown to be useful in analyzing nonlinear response of various complex fluids such as polymers, emulsions, suspensions and gels. In this Chapter, a brief description of large amplitude oscillatory shear (LAOS) was provided. Due to advances in instrumentation and experimental tools, it is possible to obtain large amount of data during LAOS. Through analysis of cyclic variation and frequency spectrum, the response can be analyzed to understand the material behaviour. Constitutive models are also being used to understand material response under LAOS.

It has been shown that LAOS can highlight the structural changes taking place in the material at large deformations. The quantification of the nonlinear response, and more importantly the physical interpretation, are still developing tools.

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References


Fig. 13 Fourier transform of point velocity time series [11] (a) x-component of velocity (b) y-component of velocity